Non-spiky density of states of an icosahedral quasicrystal

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Abstract

The density of states of the ideal three-dimensional Penrose tiling, a quasicrystalline model, is calculated with a resolution of 10 meV. It is not spiky. This falsifies theoretical predictions so far, that spikes of width 10-20 meV are generic for the density of states of quasicrystals, and it confirms recent experimental findings. The qualitative difference between our results and previous calculations is partly explained by the small number of **k** points that has usually been included in the evaluation of the density of states of periodic approximants of quasicrystals. It is also shown that both the density of states of a small approximant of the three-dimensional Penrose tiling and the density of states of the ideal two-dimensional Penrose tiling do have spiky features, which also partly explains earlier predictions.

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1 Introduction

Since the discovery of quasicrystals (QC's) [1], it has been an important issue in condensed-matter physics to find out which properties distinguish this type of material, which has long-range order but no lattice periodicity, from crystals and amorphous materials. Theoretically this problem was studied by means of so-called approximants. An approximant is a lattice periodic crystal with a large unit cell with a structure close to that of a QC. For icosahedral QC's approximants are obtained if in a higher dimensional description of a QC [2], the golden mean $\tau = \frac{1}{2}(\sqrt{5}+1)$ is approximated by a fraction. By approaching τ in a systematic way, a series of approximants can be obtained with ever larger unit cells and ever better structural convergence with respect to the ideal QC. By studying such a series of approximants and meanwhile monitoring convergence with respect to unit-cell size, results may be obtained that are valid for an ideal QC. Due to computational limitations most *first principles* calculations [3, 4, 5, 6] were restricted to so-called 1/1 approximants, where the fraction indicates the approximation made for τ, with, depending on the particular QC, approximately 150 atoms per unit cell. These calculations were done by means of the linear muffin-tin orbital (LMTO) method. They led to the surprising prediction that the electronic density of states (dos) of QC's is spiky, a property that would be specific for QC's. It started in 1989, when Fujiwara [3] predicted on the basis of a calculation for 1/1 AlMn that the dos of crystalline

and quasicrystalline AlMn consists of a set of spikes. In 1993, he found that the electronic dos of 1/1 AlMn [4, 5] and 1/1 AlCuLi [4] has dense spiky peaks of width 10-20 meV or less, which in his view suggested that spikes are generic in QC's and their crystalline approximants. In the same year, Hafner and Krajčí [7] conjectured on the basis of results for 1/1 AlZnMg that the dos of an ideal QC is spiky. In 1994, De Laissardière and Fujiwara [6] found spikes of width 14 meV in 1/1 ALCuFe. They stressed that the spikes are in the first place a consequence of quasiperiodicity, accentuated by the presence of transition metal atoms. In 1995, Krajčí and co-workers [8] found a spiky dos for 1/1 AlPdMn and 2/1 AlPdMn. The latter dos was obtained by folding the eigenvalues of the Hamiltonian at the Γ-point with a Gaussian of width 25 meV. Apart from being interesting, it was indicated that spikes may also be relevant to electronic transport in QC's [9, 5, 6]. Disappointingly spikes have not been observed directly in experiments, although a sufficiently high resolution was obtained by amongst others Stadnik and co-workers [10, 11] by means of ultrahigh energy resolution photoemission spectroscopy (5 meV), Dadydov and co-workers [12] in tunnelling experiments (1 meV) and Escudero and co-workers [13] in point contact and tunnelling experiments (0.35 meV). By convoluting the dos of 1/1 AlCuFe [6] with a Gaussian of full width at half maximum of 31.6 meV, Stadnik and co-workers [11] showed that even at a relatively low resolution, spiky features should according to the prediction be observed near the Fermi level. In ref. 14 we gave an overview of explanations that have been proposed for the discrepancy between theory and experiment, which we will not repeat here. Instead, we will focus on two explanations. The first was proposed by Hafner and Krajčí [15]. They indicated the possibility that spikes are specific for small periodic approximants of QC's and do not persist in ideal QC's. The second explanation is that spikes are an artefact of the calculation [11, 16]. We have studied these explanations by calculating the dos for the two-dimensional (2D) and the three-dimensional (3D) Penrose tiling, which are quasicrystalline model systems. The 3D Penrose tiling has icosahedral symmetry and is the basis framework for many realistic models of icosahedral QC's [3, 7, 17, 15, 5]. It is important to realise that these models do not take into account different kinds of electrons, nor do they represent realistic local atomic configurations in QC's, but they are quasiperiodic, and as a consequence of their simplicity it is possible to calculate properties of high approximants. Whereas in most LMTO studies results extrapolated for the quasiperiodic limit are based on calculations for a 1/1 approximant, we could calculate the dos of the 3D Penrose tiling with a resolution of 10 meV, a result valid in the quasiperiodic limit. In this letter, we show that spikes present in a small approximant of the 3D Penrose tiling, do not survive in the ideal QC, in agreement with the original suggestion of Hafner and Krajčí [15]. This result falsifies the prediction that all QC's have a spiky dos.

2 Model

For the 2D Penrose tiling, we have considered the same model as in ref. 14. The 3D Penrose tiling [18] is made with the cut-and-project method [2]. We consider three types of approximants. First of all, if in the internal space τ is approximated by F_{n+1}/F_n with F_i a Fibonacci number, then a so-called a periodic F_{n+1}/F_n approximant is obtained. If F_{n+2} is even, there is a body centring [2]. Second, if in the internal space an additional translation is made along a vector $(1/F_n)$ $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, another F_{n+1}/F_n approximant is formed, which has a non-symmorphic cubic space group, *e.g.*, $Pa\bar{3}$. We will refer to these approximants as cubic approximants. Finally, taking different approximations for τ in different directions in the internal space, we consider $\tau_x = F_n/F_{n-1}$, $\tau_y = F_{n+1}/F_n$ and $\tau_z = F_{n+2}/F_{n+1}$. This gives non-cubic $(F_n/F_{n-1},\ F_{n+1}/F_n,\ F_{n+2}/F_{n+1})$ approximants, of which the lattice is body-centred orthorhombic. An important parameter for each approximant is N, the number of vertices of the approximant tiling per unit cell. We studied the so-called vertex model, which has one electronic basis state on each vertex and nearest neighbour hopping via the edges of the tiling. We chose the on-site energy to be zero. The electronic basis states can be thought of as s-electrons. The Hamiltonian is:

$$H = \sum_{nm} |n\rangle\, T_{nm}\, \langle m| + \sum_{n} |n\rangle\, V_n\, \langle n|\,, \tag{1}$$

with $V_n = 0$ and $T_{nm} = 1$ eV if the vertices n and m are connected by an edge of the tiling and zero otherwise. This model has been studied before [19, 20, 21, 22], but so far it was not possible to draw definitive conclusions about the nature of the spectrum. Krajčí and Fujiwara [20] have shown that at $E = 0$ there are infinitely many, strictly localised states. An important symmetry of this model is the bipartite property [21, 14], as a consequence of which the density of states is symmetric with respect to $E = 0$ [19, 20, 21]. Also, for the non-body-centred cubic and for the non-cubic approximants, the bipartiteness of the lattice can be used to reduce the problem of finding eigenvalues of H from an $N \times N$ problem to an $N/2 \times N/2$ problem [21].

3 Method

In order to determine the dos, we perform a bandstructure calculation. Here N_k, the number of $\mathbf{k}$ points calculated in the asymmetric unit, is important. For the evaluation of the dos, we follow roughly the same scheme as in ref. 14: First we calculate the exact average dos of a linearly interpolated [23] bandstructure of an approximant in intervals of width 0.2 meV, where the averaging ensures uniform convergence [24]. Then we convolute with a Gaussian of full width at half maximum of typically 10 meV, which reduces the error in the dos by smearing away all features on a scale smaller than 10 meV including effects of the finite averaging interval of 0.2 meV, but which does not smear away spikes of width 10-20 meV. This last step is not general practice, but we will argue that it is useful.

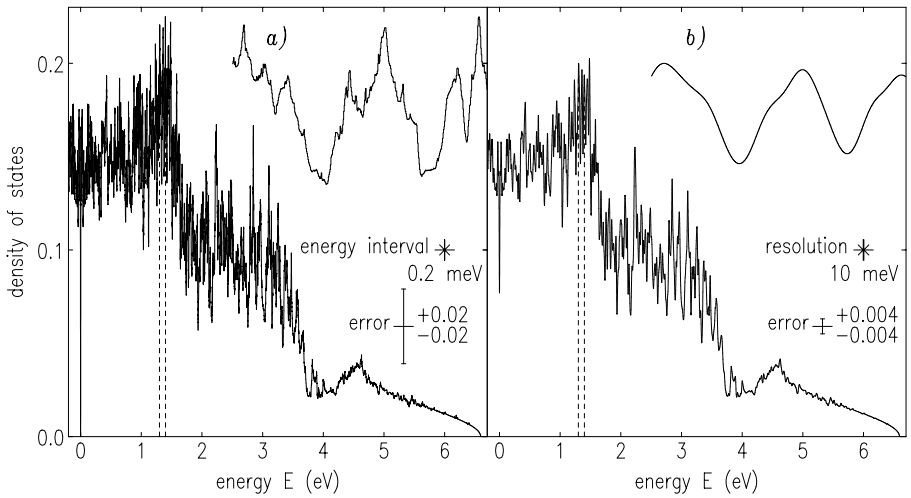

Figure 1: The density of states of the cubic 3/2 approximant of the three-dimensional Penrose tiling *a)* before and *b)* after smoothening. The inset clarifies the energy range 1.3 eV to 1.4 eV.

Maximal errors for the dos of approximants were extrapolated by making a systematic comparison of the results for various N_k and simultaneously assuming asymptotic behaviour: the error in the dos at a certain energy is the integral between the true constant energy surface and the polyhedron approximating it [25], which in three dimensions converges as $N_k^{-2/3}$ [25] for sufficiently large N_k. For an ideal tiling, the maximal error was extrapolated assuming that the asymptotic behaviour of the error is proportional to $1/N$ in a given series of approximants [26], which holds provided that the error with respect to N_k is negligible, which was checked explicitly.

4 Results

Figure 1 shows the dos of the cubic 3/2 approximant of the 3D Penrose tiling with $N = 576$ and $N_k = 1376$. It has space group $Pa\bar{3}$. A grid of so-called special $\mathbf{k}$ points [27] was used. Figure 1*a)* shows the result before convolution with a Gaussian: there are many densely distributed spikes, but the error is so large that it is not possible to say whether these spikes are real or an artefact connected to the small value of N_k. After smoothening, fig. 1*b)* is obtained. The error is considerably smaller, so that conclusions can be drawn about the spikes. Comparing the error and the amplitude of some of the spiky features, we see that certainly some of these features are real. So, the dos of small approximants of icosahedral QC's may have sharp features. In fig. 2, the dos of the ideal 2D Penrose tiling is shown. It was calculated with $N = 167761$ and $N_k = 3$,

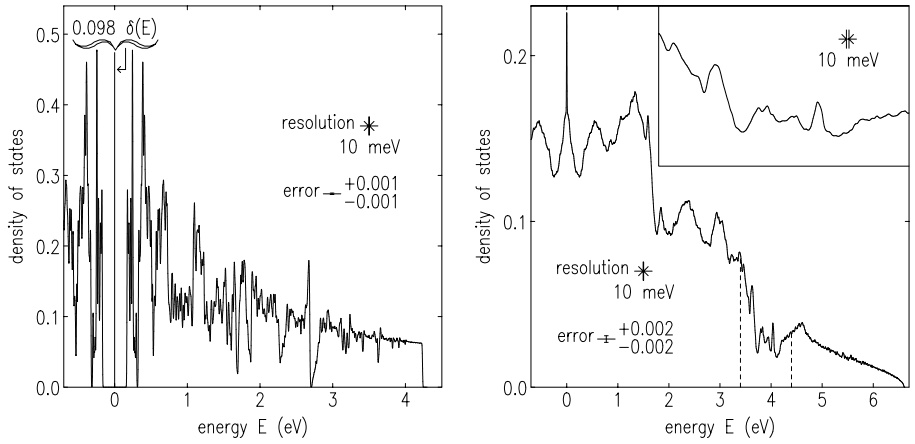

Figure 2: The density of states of the ideal two-dimensional Penrose tiling. The delta peak at $E = 0$ is not smoothened.

Figure 3: The density of states of the ideal three-dimensional Penrose tiling. The inset shows the density of states in the energy interval 3.4 eV to 4.4 eV.

where **k** points were chosen that give real phase factors. The error indicates convergence with respect to both N and N_k. Our conclusion of ref. 14, that the 2D Penrose tiling has a spiky dos, is confirmed. In fig. 3, the dos of the 3D Penrose tiling is shown. Actually, it is the dos of the non-cubic (8/5, 13/8, 21/13) approximant with $N = 21892$ and $N_k = 260$, where the **k** points lie on a regular grid which includes the Γ point, but convergence with respect to N was checked. As far as our data can tell, this result does not depend on the sequence of approximants that is considered. For example, the 8/5 approximant with $N = 10336$ and $N_k = 8196$ has a dos that deviates less than 0.008 from the graph of fig. 3 for all energies except $E = 0$. Unfortunately, the 13/8 approximant with $N = 43784$ is too large for us in order to be able to compute a sufficient number of **k** points. Since the dos of the ideal 3D Penrose tiling in fig. 3 appears to be quite smooth, we conclude that the spikes of fig. 1*b)* do not survive in the quasiperiodic limit. Figure 4*a)* [t] gives the dos of the non-cubic (3/2, 5/3, 8/5) approximant of the 3D Penrose tiling with $N = 1220$ and $N_k = 36$. The number of electronic basis states per unit cell and N_k were chosen as close as possible to those of the calculation for icosahedral AlCuFe [6], and we chose the same width for the Gaussian as Stadnik and co-workers [11] did when smoothening it. Figure 4*b)* shows the same dos with $N_k = 16388$. Comparing the two graphs, we see that taking into account a too small number of **k** points may well lead to quite broad ($\sim$ 32 meV) additional features in the dos. These features then are an artefact. Because of the indicated error in fig. 4*a)* it is clear these features should not be taken seriously. The prediction for AlFeCu of ref. 6 does not indicate an error and from the published data it is

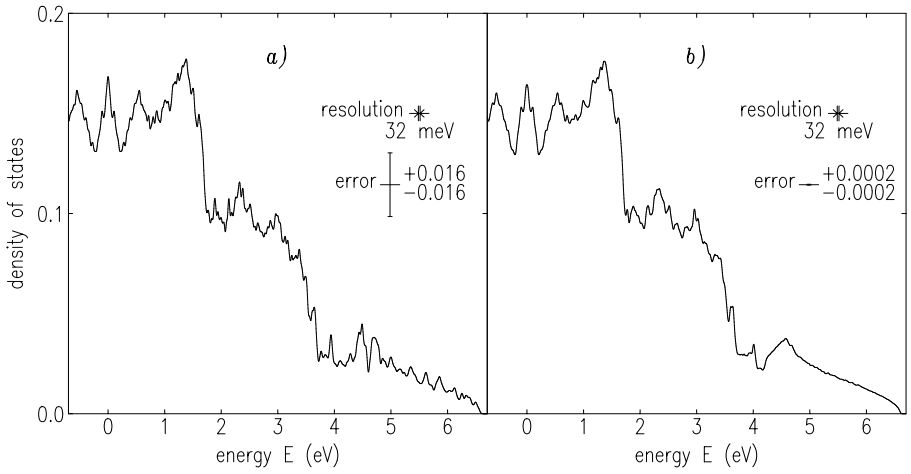

Figure 4: The density of states of a (3/2, 5/3, 8/5) approximant of the three-dimensional Penrose tiling with *a)* $N_k = 36$ and *b)* $N_k = 16388$.

not clear whether the predicted spikes are an artefact or not. A too small N_k may well explain some of the spikes predicted in literature. Expressly, we want to remark that it is in principle legitimate to try to keep the number of **k** points that are calculated, small in order to save limited computer resources, but one has to realise the price that is paid: either the error is larger or the data should be presented with a worse resolution.

5 Conclusions

We have carried out an analysis of the influence of the size of the approximant unit cell and the number of $\boldsymbol{k}$ vectors in the Brillouin zone on the finer features of the electronic dos in an icosahedral tight-binding model. We have shown that the dos of the 2D Penrose tiling is spiky (fig. 2), whereas the dos of the icosahedral 3D Penrose tiling is smooth (fig. 3), at the given resolution of 10 meV. We have also shown how a spiky dos would be predicted for our 3D model when (*i*) only a small periodic approximant would have been studied (fig. 1*b*) or (*ii*) a too small number of **k** points would have been taken into account in the calculations, leading to large numerical errors (fig. 4). Possibly the published calculations predictions that spikes are generic for icosahedral QC's, have not sufficiently taken these two points into account. Our results further suggest that although experimentally spikes could not be observed in QC's, they might be found in approximant phases.

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